SYNTHESIS OF FUEL ALCOHOLS AND MTBE FROM SYNGAS USING SPINEL OXIDE BASED CATALYSTS

David M. Minahan, Walter M. Hart
Technical Center, Union Carbide Corporation, P.O. Box 8361, South Charleston, WV 25303

William S. Epling and Gar B. Hoflund
Department of Chemical Engineering, University of Florida, Gainesville, FL 32611

ABSTRACT

An equal mole mixture of methanol and isobutanol produced from syngas would be an ideal for the production of MTBE for use as a gasoline additive. The best present day syngas to alcohols catalysts and catalyst systems make too much methanol to be economically attractive, with typical methanol/isobutanol mole ratios of 3 or greater. We have investigated a Zn/Cr commercial methanol synthesis catalyst promoted with potassium and find that it is very selective for isobutanol when run under high temperature (> 400 C) and high pressure (>1000 psi) conditions due to both kinetic and thermodynamic considerations. Isobutanol rates >100 g/kg-hr are observed with a methanol/isobutanol mole ratio of 1.9. Surface characterization (via ISS and XPS) shows that the surface of the catalyst changes upon reduction and with use. Movement of potassium and chromium within the surface and near surface region of the catalyst is observed which can be correlated with catalytic performance
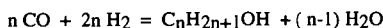
INTRODUCTION

Oxygen-containing hydrocarbon compounds can be added to gasoline to both reduce emissions and increase the octane rating of the fuel. Typical additives that have been examined are ethers such as MTBE and TAME and alcohols such as methanol. Methanol can be produced from syngas in high selectivity and can be used as an octane enhancer, but addition to gasoline can cause problems: the presence of water can cause phase separation and the Reid vapor pressure of the mixture is increased, leading to increased emissions from the gas tank. Mixtures of methanol and higher alcohols are a better alternative to methanol alone as ethanol raises the octane rating of the fuel and higher alcohols act as co-solvents, minimizing phase separation and lowering the overall vapor pressure of the additive. For long chain alcohols, branched alcohols are preferred over linear alcohols for enhancing the octane rating, whilst linear alcohols are preferred over branched alcohols for co-solvency characteristics. Ethers such as MTBE and TAME are preferred as additives due to their excellent co-solvent properties, lower volatility as compared with methanol and ethanol and their octane enhancing properties. Nonetheless, branched alcohols such as isobutanol and its higher homologs would still be of interest in their own right or as potential precursors to accepted additives such as MTBE or TAME. Alternatively, an equimolar mixture of methanol and isobutanol could be used as a direct precursor for the manufacture of MTBE.

Higher alcohol synthesis (HAS) catalysts have primarily evolved from modified methanol synthesis catalysts. The original methanol synthesis catalysts were based on a zinc/chromium spinel oxide operated around 400°C, and could tolerate some sulfur impurities in the syngas feed [1]. With the advent of effective desulfurization techniques for the syngas, a second generation methanol synthesis catalyst was developed, based on a more active copper metal based formulation which could operate at substantially lower temperatures (250-300°C) [2]. In both cases, the addition of alkali to the system resulted in the formation of higher alcohols, albeit at a substantially lower overall productivity. Other catalyst systems have been developed based on molybdenum sulfide (Dow/Union Carbide) [3], supported rhodium metal (Union Carbide) [4] and supported Cu/Co clusters (IFP) [5]. Once again, alkali is commonly added to the formulations. An interesting contrast between "modified methanol" catalysts and other systems is in the types of alcohols produced: the "modified methanol" catalysts produce mainly branched alcohols with a non Anderson-Schulz-Flory (ASF) distribution via an aldol condensation mechanism, the major products being methanol and isobutanol. The others produce linear alcohols via classical CO insertion/hydrogenation, producing the characteristic ASF distribution similar to that observed in linear condensation polymerization.

The following major reactions can take place over the catalyst or tube walls:
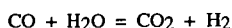
Alcohol Formation

$$n\ CO\ +\ 2n\ H_2\ =\ C_nH_{2n+1}OH\ +\ (n-1)\ H_2O$$

Hydrocarbon Formation

$$nCO\ +\ (2n+1)\ H_2\ =\ C_nH_{2n+2}\ +\ n\ H_2O$$
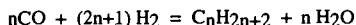
Water-Gas-Shift Reaction Equilibrium

$$CO\ +\ H_2O\ =\ CO_2\ +\ H_2$$

Boudouard Reaction (CO disproportionation)

$$2CO\ =\ C\ +\ CO_2$$

Catalyst Selection and Testing Protocol

The catalysts examined here are materials consisting of a spinel oxide support (general formula AB_2O_4, where $A = M^{2+}$ and $B = M^{3+}$), promoted with potassium. The spinel itself consists of the traditional zinc/chromium oxide formulation, modified by the inclusion of excess zinc oxide and was obtained from Engelhard Corporation. The catalysts were tested first at low temperatures in stainless steel reactor tubes, then at higher temperatures (> 340 °C) in copper lined tubes to avoid the Boudouard reaction and hydrocarbon formation, known to be catalyzed by stainless steel (Fe, Ni) at these higher temperatures.

Reaction Mechanism

HAS requires at least two complimentary, yet competing reactions: carbon-carbon bond formation and hydrogenation. In the copper metal based, low temperature system, carbon-carbon bond formation is thought to occur via a classical CO insertion mechanism, followed by hydrogenation. In contrast, the high temperature catalysts utilize an aldol condensation mechanism to form the carbon-carbon bonds. The aldol reaction can proceed via acid or base catalysis.

The selection of elements other than copper as hydrogenation catalysts is a crucial feature of the high temperature formulations. Copper cannot be used as it sinters rapidly above 300°C, resulting in catastrophic loss in activity. Thus, temperature cannot be used as a lever in a copper catalyst system in order to improve alcohol activity. Nonetheless, both kinetics and thermodynamics favor HAS at higher temperatures. Methanol synthesis is at equilibrium under reaction conditions and higher alcohols are formed by consecutive reactions from methanol, thus higher temperatures will accelerate the secondary, higher alcohol forming reactions while the equilibrium of the methanol synthesis implies lower methanol concentrations. The net result is a considerable improvement in both the rate and selectivity to higher alcohols at higher temperatures at the expense of methanol. However, higher temperatures also enhance the formation of methane and higher hydrocarbons, so overall catalyst acidity must be carefully controlled. Thus alkali addition (in the form of potassium) helps by both providing basic sites for higher alcohol synthesis via the base-catalyzed aldol condensation and by neutralizing acid sites responsible for hydrocarbon formation.

The thermodynamic equilibrium for methanol formation dictates that methanol concentration grows quadratically with total pressure, while the concentration of higher alcohols exhibits a weaker dependence, resulting from kinetic considerations. Thus, pressure does increase reaction rate, but is not an effective handle for boosting HAS vs. methanol. However, hydrocarbon production is minimized at higher pressures, so total alcohol selectivity should rise.

RESULTS & DISCUSSION

Experiments were run in two different reactors. At lower temperatures (≤340°C) we used a stainless steel tubular microreactor. Low temperature runs were conducted at 12000 GHSV, $H_2/CO=1$ and 1000 psig. Most experiments were run in duplicate.

Low Temperature Operation (up to 340°C): The results are displayed in Table 1 below:

Table 1
K-impregnated Zn/CrO Catalysts - Low Temperature Operation

Temperature (°C)	260			
Potassium Loading	0% K	1% K	3% K	5% K
%CO2-free MeOH Selectivity	92	88	55	59
%CO2-free HC Selectivity	8	12	43	35
%CO2-free ROH Selectivity	92	88	57	65
%CO2-free C2+ ROH Selectivity	0	0	2	6
Isobutanol Rate (g/kg-hr)	0	0	0	0
Total Alcohol Rate (g/kg-hr)	206	104	35	20
Methanol Rate (g/kg-hr)	206	104	34	19
n-Propanol Rate (g/kg-hr)	0	0	0	0
Hydrocarbon Rate (g/kg-hr)	9	7	12	6
% CO Conversion	0.1	0.7	3.5	1.1

Temperature (°C)	300			
Potassium Loading	0% K	1% K	3% K	5% K
%CO2-free MeOH Selectivity	77	57	41	29
%CO2-free HC Selectivity	20	28	44	52
%CO2-free ROH Selectivity	80	72	56	48
%CO2-free C2+ ROH Selectivity	3	15	15	19
Isobutanol Rate (g/kg-hr)	0	0	0	0
Total Alcohol Rate (g/kg-hr)	327	197	99	73
Methanol Rate (g/kg-hr)	318	170	77	50
n-Propanol Rate (g/kg-hr)	4	14	10	9
Hydrocarbon Rate (g/kg-hr)	39	40	40	43
% CO Conversion	3.6	6.7	5.5	3.6

Temperature (°C)	340			
Potassium Loading	0% K	1% K	3% K	5% K
%CO2-free MeOH Selectivity	56	37	23	13
%CO2-free HC Selectivity	39	50	61	64
%CO2-free ROH Selectivity	61	50	39	36
%CO2-free C2+ ROH Selectivity	5	13	16	23
Isobutanol Rate (g/kg-hr)	0	0	0	3.7
Total Alcohol Rate (g/kg-hr)	428	361	197	177
Methanol Rate (g/kg-hr)	405	288	134	84
n-Propanol Rate (g/kg-hr)	7	34	31	45
Hydrocarbon Rate (g/kg-hr)	134	190	172	191
% CO Conversion	11.2	17.4	15.1	20.7

In all cases, higher alcohol production was low. Isobutanol was observed only for the case with the highest potassium loading (5%) at the highest temperature (340 °C). CO conversion increased with temperature as expected. Although higher temperatures increased methanol, total alcohol and total hydrocarbon activities, higher temperatures also promoted hydrocarbon formation at the expense of methanol synthesis. C2+ alcohol selectivity appeared to increase from 260 °C to 300 °C, but a further increase in temperature (to 340 °C) did not result in a corresponding increase in selectivity, probably due to interference from the stainless steel reactor walls. Catalysts impregnated with potassium had higher C2+ alcohol selectivity than the bare support at all three temperatures, and C2+ alcohol selectivity increased with potassium loading. However, total alcohol rates decreased as the loading of potassium on the catalyst increased due mostly to the suppression of methanol synthesis.

These results led us to believe that even higher operating temperatures would be beneficial, provided unwanted side reactions catalyzed by the stainless steel reactor walls could be eliminated. Further tests were performed in copper lined tubes. It should be noted that reaction *rates* are not dramatically increased by increased temperatures, rather the product distribution between methanol/higher alcohols and hydrocarbons is shifted; it seemed prudent,

therefore, to explore the use of higher pressures as a means of boosting reaction rates, so pressures in excess of 1000 psig were also examined.

High Temperature/High Pressure Operation (400°C and above, up to 1500 psig): The results at 12000 GHSV and $H_2/CO = 1$ are displayed in Table 2 below:

Table 2
K-impregnated Zn/CrO Catalysts - High Temperature Operation

Catalyst	Unpromoted Spinel			
Temperature (°C)	400	400	440	440
Pressure (psig)	1000	1500	1500	1000
%CO2-free ROH Selectivity	65	77	43	27
Total Alcohol Rate (g/kg-hr)	111	236	133	59
Methanol Rate (g/kg-hr)	105	223	102	41
n-Propanol Rate (g/kg-hr)	0	0	18	10
Isobutanol Rate (g/kg-hr)	6	13	13	5
MeOH/I-BuOH Mole Ratio	73	68	31	36
Hydrocarbon Rate (g/kg-hr)	30	35	94	86

Catalyst	1% Potassium			
Temperature (°C)	400	400	440	440
Pressure (psig)	1000	1500	1500	1000
%CO2-free ROH Selectivity	61	75	53	53
Total Alcohol Rate (g/kg-hr)	133	251	167	129
Methanol Rate (g/kg-hr)	78	170	49	70
n-Propanol Rate (g/kg-hr)	8	0	9	6
Isobutanol Rate (g/kg-hr)	47	81	103	47
MeOH/I-BuOH Mole Ratio	6.6	8.4	1.9	6.0
Hydrocarbon Rate (g/kg-hr)	48	46	101	6

Catalyst	3% Potassium			
Temperature (°C)	400	400	440	440
Pressure (psig)	1000	1500	1500	1000
%CO2-free ROH Selectivity	80	88	70	70
Total Alcohol Rate (g/kg-hr)	75	159	99	67
Methanol Rate (g/kg-hr)	38	92	26	8
n-Propanol Rate (g/kg-hr)	4	10	0	0
Isobutanol Rate (g/kg-hr)	34	57	67	57
MeOH/I-BuOH Mole Ratio	4.5	6.4	1.5	0.54
Hydrocarbon Rate (g/kg-hr)	11	12	29	21

Catalyst	5% Potassium			
Temperature (°C)	400	400	440	440
Pressure (psig)	1000	1500	1500	1000
%CO2-free ROH Selectivity	96	97	84	83
Total Alcohol Rate (g/kg-hr)	82	159	130	70
Methanol Rate (g/kg-hr)	59	123	47	16
n-Propanol Rate (g/kg-hr)	0	0	23	10
Isobutanol Rate (g/kg-hr)	23	34	51	38
MeOH/I-BuOH Mole Ratio	10	14	3.7	1.7
Hydrocarbon Rate (g/kg-hr)	2	3	15	10

The non-promoted catalyst gives mostly methanol and a small amount of isobutanol. The total alcohol rate more than doubles when the pressure is increased from 1000 to 1500 psig, showing the beneficial effect of pressure on reaction rate. Increasing the temperature to 440°C cuts the totoal alcohol selectivity and the methanol rate in half and almost triples the hydrocarbon rate.

1% potassium promotion does not substantially affect total alcohol selectivity, but the alcohol distribution shifts dramatically in favor of isobutanol. Isobutanol rates >100 g/kg-hr are observed at the highest operating conditions of temperature and presssure (440°C and 1500 psig) with a methanol/isobutanol mole ratio of 1.9. Total alcohol selectivities are above 50%.

Increasing the level of potassium on the catalyst results in an increase in selectivities to total alcohols, but a decrease in total alcohol rate. A methanol/isobutanol mole ratio < 1 (0.54) can be obtained for the 3 wt% potassium catalyst at 440°C and 1000 psi, but the isobutanol rate is reduced to < 60 g/kg-hr. The 5 wt% material is the most selective for alcohols, but the methanol rate has increased and the isobutanol rate has decreased.

Surface Science Characterization

Surface characterization (via ISS and XPS) shows that the surface of the catalyst changes upon reduction and with use. Reduction under hydrogen (250°C for 4.5 hrs in 1 x 10-7 torr hydrogen) induces the migration of potassium to the topmost monolayer resulting in complete surface coverage as observed by ion scattering spectroscopy (ISS). X-ray photoelectron spectroscopy (XPS) data are consistent with these observations and also reveal that the near-surface region of the catalysts consist primarily of zinc oxide. Chromium is observed, and appears to be present as potassium chromate or potassium dichromate.

The used catalysts exhibit a potassium rich surface, but the near surface contains much less potassium and again consists essentially of zinc oxide. The chromium now appears to be present as chromium(III) oxide, hydroxide and some chromium metal. These results suggest that the active phase of the catalyst is potassium supported on zinc oxide, possibly promoted with chromium.

ACKNOWLEDGMENTS

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